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Title: US-DOE NWAL Support to ESL for 241Am/241Pu Age Dating: Safeguards Technology Project Overview for the IAEA

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Los Alamos NATIONAL LABORATORY

US-DOE NWAL Support to ESL for ^{241}Am/^{241}Pu Age Dating: Safeguards Technology Project Overview for the IAEA

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June 23, 2021

NNSA National Nuclear Security Administration
OFFICE OF NONPROLIFERATION AND ARMS CONTROL (NPAC)
INTERNATIONAL NUCLEAR SAFEGUARDS

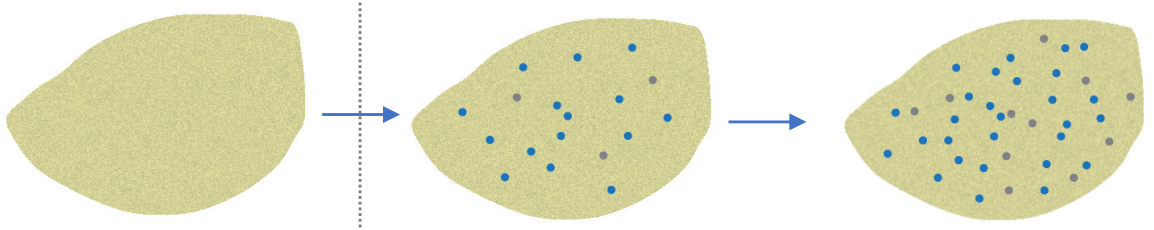
Project Motivation - IAEA

IAEA Priority Objective T2, R&D Need T.2.R6 to “Develop and implement methods to detect signatures of nuclear activities in environmental samples including: Age determination of U and Pu relevant to the origin of nuclear materials” - specific focus on plutonium (Pu) age dating

How is a Pu model age produced and measured?

model age = purification date if assumptions are met

Picture from Wayne et al. 2018 Journal of Nuclear Materials

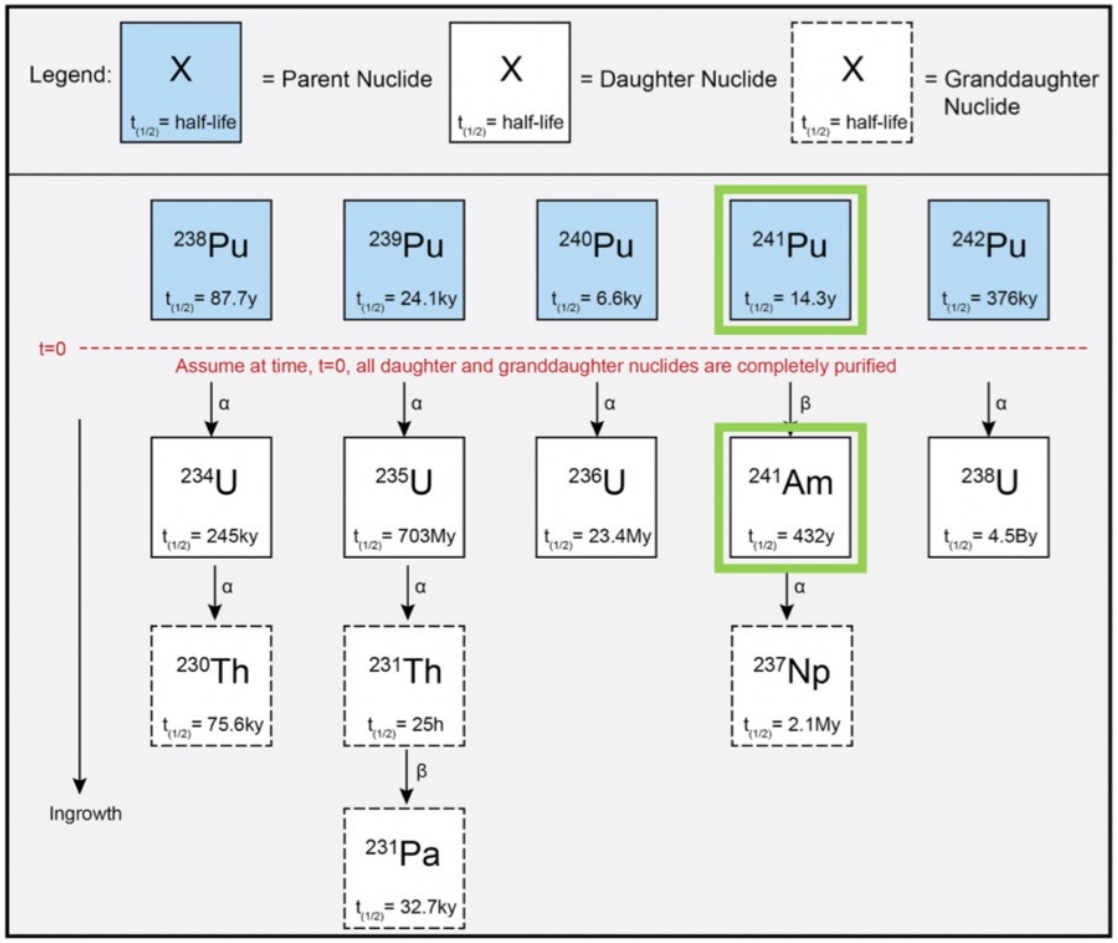


Model Assumption 1
At time of production, t=0, **only parent Pu nuclides**

Time increases from t=0

Model Assumption 2
As time passes, daughter and granddaughter nuclides ingrow and decay
no loss or gain of parent-daughter-granddaughter

Project Motivation - IAEA



There are multiple chronometers that can be used to age date Pu

Within US-DOE NWAL, capability to use ***ALL*** chronometers shown for bulk Pu

2019 RANC Conference:
IAEA ESL developing ^{241}Am capability – both radiochemistry to separate ^{241}Am and mass spectrometry to measure ^{241}Am/^{243}Am ratios

Project focuses on ^{241}Am/^{241}Pu chronometer based on IAEA requests and to align with ongoing development at ESL

Project Motivation - IAEA

Pu age dating is especially challenging for IAEA cotton swipe matrix… U blank, Pu mixed with U sources (U chronometers may be affected), Pu present in very small concentrations (fg – pg) ; therefore, decay products present in concentrations near limit of detection or below

Photo: Environmental swipe kit, iaea.org, Nuclear Verification Series No. 1 (Rev. 2)

^{241}Pu

$t_{(1/2)}$ = 14.3y

^{241}Am

$t_{(1/2)}$ = 432y

Pu Decay to Am offers a clock for age dating

Project Motivation – Specific to US-DOE NWAL

US-DOE NWAL

Los Alamos NATIONAL LABORATORY

Lawrence Livermore National Laboratory

OAK RIDGE National Laboratory

Pacific Northwest NATIONAL LABORATORY

^{241}Pu Assay: methods verified through IAEA blind QC program and through US-DOE NWAL QC cotton swipes

^{241}Am Assay: IAEA to US-DOE requests…

29 bulk ES requests, 22 since 2018, increased need

- 2011: 4
- 2014: 2
- 2016: 1
- 2018: 2
- 2019: 15
- 2020: 2
- 2021: 3 (ongoing…)

No previous method validation / proficiency testing program for ^{241}Am measurements

No previous intercomparison of techniques between US-DOE NWAL laboratories

Challenges – Measurement of ^{241}Am, Pu Age Dating

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and Safeguards Unit

CERTIFIED REFERENCE MATERIAL
IRMM – 0243

CERTIFICATE OF ANALYSIS

AMERICIUM IN NITRIC ACID SOLUTION		
	Amount content	
	Certified value [1] [nmol/g (solution)]	Uncertainty [2] [nmol/g (solution)]
^{243}Am	5.696	0.011
	Isotope amount ratio	
	Certified value [1] [mol/mol]	Uncertainty [2] [mol/mol]
$n(^{241}\text{Am})/n(^{243}\text{Am})$	0.136138	0.000054

[1] The certified values are traceable to the International System of units (SI) via the values on the respective certificates of IRMM-049d and IRMM-290b-A3 and via the half-life of ^{241}Pu. The reference date for the certified values is January 1, 2017.
[2] The uncertainty is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

There is no minimum sample intake to be taken into account.

The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out.

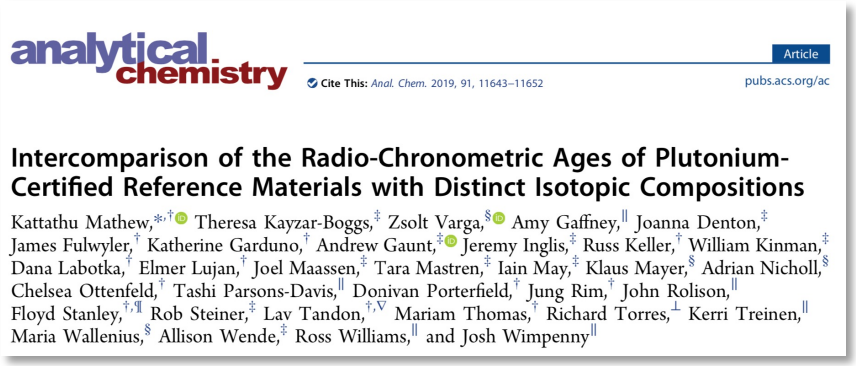
Measurement of ^{241}Am by isotope dilution mass spectrometry with a ^{243}Am tracer requires an instrument bias & gain correction…

No Am isotope composition certified reference materials (CRMs) with certified ^{241}Am/^{243}Am
Workaround – use IRMM-0243, ***but how***?
Bias/gain or as a quality control?

Options:
Use U for mass bias/gain
Use Pu for mass bias/gain
Use Am for mass bias/gain
*biases have been observed between systems and standards

^{241}Am may be at/near limit of detection in young samples

Challenges – Measurement of ^{241}Am, Pu Age Dating



analytical chemistry

Article

Cite This: *Anal. Chem.* 2019, 91, 11643−11652

pubs.acs.org/ac

Intercomparison of the Radio-Chronometric Ages of Plutonium-Certified Reference Materials with Distinct Isotopic Compositions

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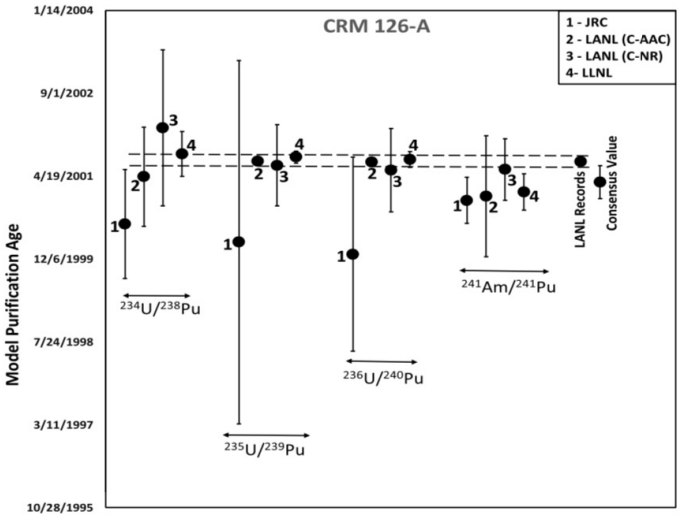


Left: Figure from Mathew et al. 2019 showing the development of a consensus age for CRM 126-A Pu metal standard using 4 different chronometers

There are no certified reference materials (CRMs) that are certified for Pu model age or purification dates…

How do you validate/QA measured Pu ages?

Community working toward "consensus ages"
Mathew et al. 2019
*included LANL and LLNL participation with EU JRC

Safeguards Technology (NA-241):
Working towards development of Pu particle reference materials (SRNL and PNNL) – these may be ideal CRM materials for Pu age dating in the future, but not currently available…

Project Task Overview

Task 1: Knowledge Exchange & Workshop

- US method exchange
- materials development
- domestic presentation
- IAEA-USDOE exchange TBD

Task 3: Report on Best Practices

- radiochemistry
- mass spectrometry
- recommendations for broader NWAL

Task 2: Experimentation and Method Optimization

- Laboratory testing based on knowledge exchange and identified challenges
- Comparison of results
- Iterative optimization of methods

Task 4: Preparation for Round-Robin Verification

- Dope blank swipes with well-characterized Pu CRMs
- Consensus Pu ages for materials from Mathew et al. 2019 can fill CRM gap

Innovation and Outcomes

- Radiochemistry and mass spectrometry expertise sharing
- First comparison of US-DOE NWAL ^{241}Am procedures and methods, method optimization for bulk ES
- Novel interlaboratory round robin to validate developed methods despite lack of reference materials
- Supports verification of safeguards declarations (IAEA Priority Objective/Need T2/T.2.R6, SGAS-002)

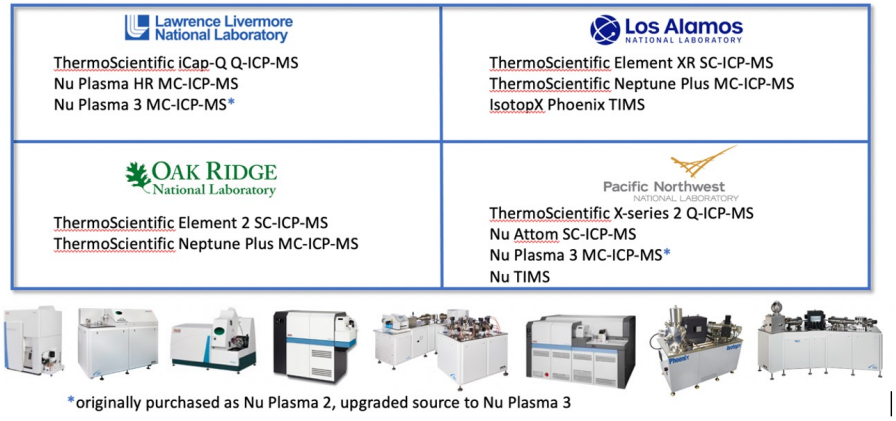
Task 1 Progress Status - Completed

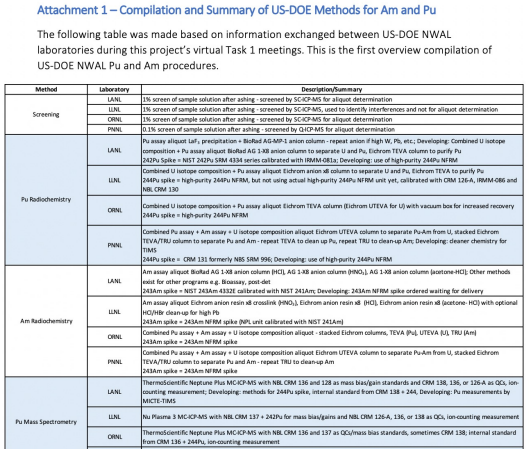
Original project goals:

1) Exchange methods for Pu age dating and discuss challenges amongst US-DOE NWAL
2) Prepare knowledge exchange materials

Progress:

- Project team held 6 virtual technical meetings to exchange methods and develop workshop materials
- Project team developed a compendium of current methods for ^{241}Am and ^{241}Pu measurements





Attachment 1 – Compilation and Summary of US-DOE Methods for Am and Pu

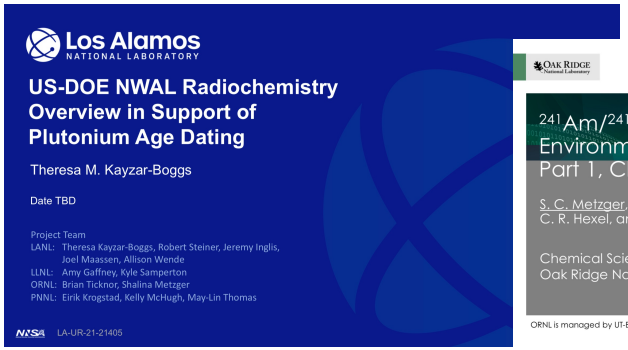
The following table was made based on information exchanged between US-DOE NWAL laboratories during this project's virtual Task 1 meetings. This is the first overview compilation of US-DOE NWAL Pu and Am procedures.

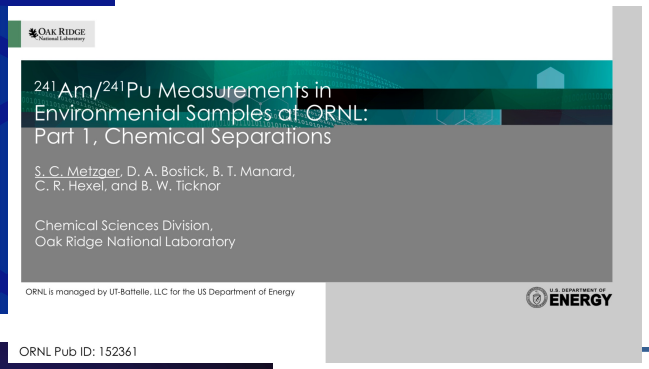
Method	Laboratory	Description/Summary
Screening	LANL	1% screen of sample solution after ashing - screened by SC-ICP-MS for aliquot determination
	LLNL	1% screen of sample solution after ashing - screened by SC-ICP-MS, used to identify interferences and not for aliquot determination
	ORNL	1% screen of sample solution after ashing - screened by SC-ICP-MS for aliquot determination
	PNNL	0.1% screen of sample solution after ashing - screened by Q-ICP-MS for aliquot determination
Pu Radiochemistry	LANL	Pu assay aliquot LaF_3 precipitation + BioRad AG-MP-1 anion column - repeat anion if high W, Pb, etc.; Developing: Combined U isotope composition + Pu assay aliquot BioRad AG 1-X8 anion column to separate U and Pu, Eichrom TEVA column to purify Pu 242Pu Spike = NIST 242Pu SRM 4334 series calibrated with IRMM-081a; Developing: use of high-purity 244Pu NFRM
	LLNL	Combined U isotope composition + Pu assay aliquot Eichrom anion x8 column to separate U and Pu, Eichrom TEVA to purify Pu 244Pu spike = high-purity 244Pu NFRM, but not using actual high-purity 244Pu NFRM unit yet, calibrated with CRM 126-A, IRMM-086 and NBL CRM 130
	ORNL	Combined U isotope composition + Pu assay aliquot Eichrom TEVA column (Eichrom UTEVA for U) with vacuum box for increased recovery 244Pu spike = high-purity 244Pu NFRM
	PNNL	Combined Pu assay + Am assay + U isotope composition aliquot Eichrom UTEVA column to separate Pu-Am from U, stacked Eichrom TEVA/TRU column to separate Pu and Am - repeat TEVA to clean up Pu, repeat TRU to clean-up Am; Developing: cleaner chemistry for TIMS 244Pu spike = CRM 131 formerly NBS SRM 996; Developing: use of high-purity 244Pu NFRM
Am Radiochemistry	LANL	Am assay aliquot BioRad AG 1-X8 anion column (HCl), AG 1-X8 anion column (HNO_3), AG 1-X8 anion column (acetone-HCl); Other methods exist for other programs e.g. Bioassay, post-det 243Am spike = NIST 243Am 4322E calibrated with NIST 241Am; Developing: 243Am NFRM spike ordered waiting for delivery
	LLNL	Am assay aliquot Eichrom anion resin x8 crosslink (HNO_3), Eichrom anion resin x8 (HCl), Eichrom anion resin x8 (acetone- HCl) with optional HCl/HBr clean-up for high Pb 243Am spike = 243Am NFRM spike (NPL unit calibrated with NIST 241Am)
	ORNL	Combined Pu assay + Am assay + U isotope composition aliquot - stacked Eichrom columns, TEVA (Pu), UTEVA (U), TRU (Am) 243Am spike = 243Am NFRM spike
	PNNL	Combined Pu assay + Am assay + U isotope composition aliquot Eichrom UTEVA column to separate Pu-Am from U, stacked Eichrom TEVA/TRU column to separate Pu and Am - repeat TRU to clean-up Am 243Am spike = 243Am NFRM spike
Pu Mass Spectrometry	LANL	ThermoScientific Neptune Plus MC-ICP-MS with NBL CRM 136 and 128 as mass bias/gain standards and CRM 138, 136, or 126-A as QCs, ion-counting measurement; Developing: methods for 244Pu spike, internal standard from CRM 138 + 244, Developing: Pu measurements by MICTE-TIMS
	LLNL	Nu Plasma 3 MC-ICP-MS with NBL CRM 137 + 242Pu for mass bias/gains and NBL CRM 126-A, 136, or 138 as QCs, ion-counting measurement
	ORNL	ThermoScientific Neptune Plus MC-ICP-MS with NBL CRM 136 and 137 as QCs/mass bias standards, sometimes CRM 138; internal standard from CRM 136 + 244Pu, ion-counting measurement

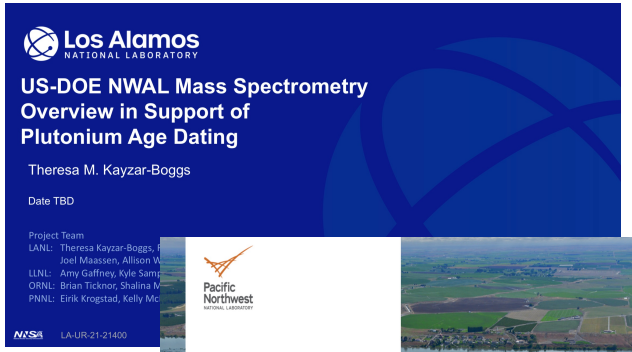
Figures from mid-year report: Far Left: summary of instrumentation platforms used across the US-DOE NWAL for ^{241}Am and ^{241}Pu measurements – ten different instrument platforms. Left: Image of appendix to mid-year report summarizing current methods for Pu age dating at LANL, LLNL, ORNL, and PNNL

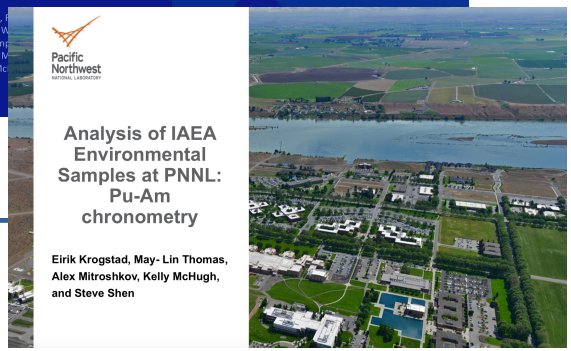
Task 1 Progress Status - Completed

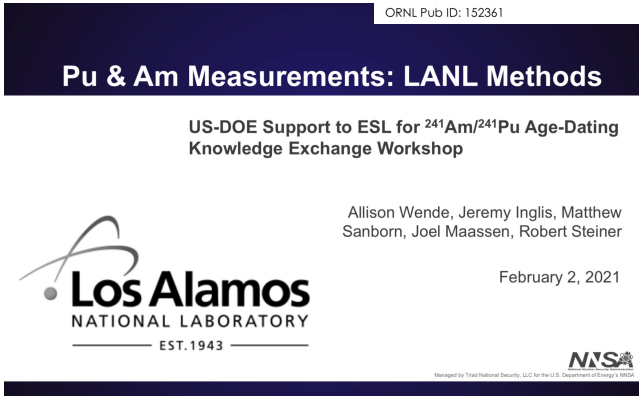
Nine reviewed and released presentations summarizing current state-of-the-art for ^{241}Am and ^{241}Pu radiochemistry and mass spectrometry methods within US-DOE NWAL

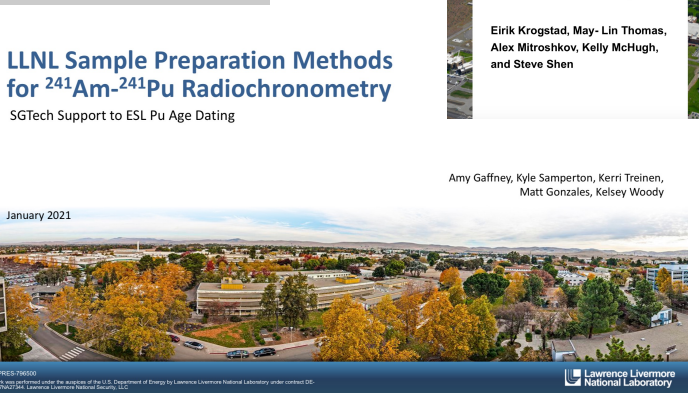












Task 1 Outcomes

Knowledge exchange between the US-DOE NWAL identified method similarities:

Radiochemistry

- Implementation of sample screening for Pu and Am aliquot size determination/design purification methods for Pu and Am from the bulk matrix
- All laboratories using/working towards the use of the high-purity ^{244}Pu nuclear forensic reference material (NFRM) and the ^{243}Am NFRM spike
- Use of Eichrom TEVA resin for Pu purifications

Mass Spectrometry

- All laboratories utilize New Brunswick Laboratory (NBL) Pu certified reference materials (CRMs) – CRM 126-A, CRM 136, CRM 137, CRM 138
- All laboratories use the new ^{243}Am CRM from the European Union's Institute of Reference Materials and Measurements (IRMM), IRMM-0243 during Am analysis

  NOTE: none of the labs use this for its intended purpose as a ^{243}Am spike

As well as common challenges:

- Low concentrations of ^{241}Am and ^{241}Pu requiring combined aliquots for radiochemistry
- Lack of Am CRMs and Pu age dating CRMs

Task 2 Progress Status – In Process

Experimentation to promote method optimization:

Radiochemistry and mass spectrometry for ^{241}Am and ^{241}Pu

Planned laboratory-based experimentation was designed based on discussions from project Task 1

Goal: Complete experiments in July 2021;
Report on Best Practices, can share with IAEA ESL

LANL:

- Compare use of U, Pu and Am CRMs for bias/gain during $^{241}Am/^{243}Am$ ratio measurements
  - Bias observed before during analysis on the ThermoScientific Element and Neptune Plus
  - Determine the best method for Am isotope ratio measurement

- Radiochemists will evaluate the feasibility of taking a combined U, Pu, Am aliquot for U isotope composition, Pu assay, and Am assay measurement, this would lower LANL's method detection limit for Am on a cotton swipe

Task 2 Progress Status – In Process

LLNL:

- Past $^{241}Am/^{243}Am$ ratio measurements have shown different biases during the use of a U mass bias standard during mass spectrometry analysis on a Nu Instruments NuPlasma MC-ICP-MS
- Experiments will be designed to explore the origin of this bias

ORNL:

- Radiochemical purifications for Pu and U at ORNL modified to minimize resin volumes used during column chemistry - yet to be done for Am purifications
- Experiments to evaluate using smaller resin column volumes during Am separations to minimize blank contributions and increase the speed of chemical purifications

PNNL:

- Discussion during Task 1 technical meetings centered on the topic of isobaric interferences during MC-ICP-MS analysis of Pu
- Experiments to evaluate elution profiles of Pu and Am during chemical purification with moderate-to-substantial levels of interferents (e.g. Pb, W)

Task 3 and 4 – Deliverable, Decision Point, Round Robin

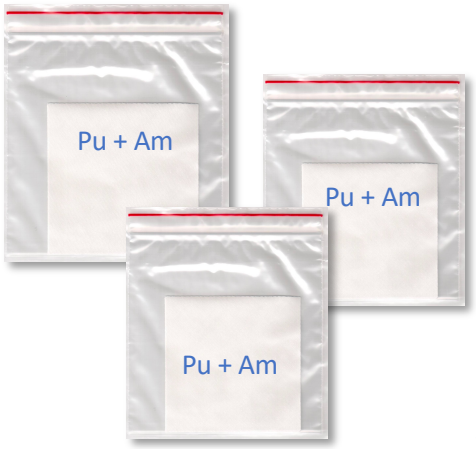
Task 3: Report on collaborative best practices for $^{241}Am/^{241}Pu$ age dating – based on results from Task 2. Report can be shared with IAEA ESL.

Task 4: Decision Point July 30, 2021 - Preparation for Round Robin?

Central challenge for age dating Pu on cotton swipes from the IAEA is that there are currently no CRMs to validate results and there are no established proficiency tests or QA/QC programs to test this capability. Proposed the development of a Round Robin exercise for FY22.

If approved, in FY21:

- Design round robin materials
  - Can dope swipes with “consensus age” material
  - Can make swipe with “designed” age using Pu + ^{241}Am CRMs
  - Plan verification of materials at LANL



Proposed Work FY22

US-DOE NWAL

If Pu age dating round robin is approved:

- Prepare and characterize "blind" round robin swipes doped with Pu CRM with consensus $^{241}Am/^{241}Pu$ model age and synthetic sample prepared from Pu CRM + ^{241}Am CRM
  - LANL has 3 NWAL chemists and 2 – 4 NWAL mass spectrometrists, will divide characterization work and round-robin execution to keep exercise unknown
- Exchange environmental swipes – shipping/receiving
- Interlaboratory (LANL, LLNL, ORNL, PNNL, +/- others?) $^{241}Am/^{241}Pu$ age dating of the bulk round robin swipe materials
- Data exchange and meeting

Primary Goal:

Intercomparison data to validate ^{241}Am measurements made by US-DOE NWAL for the IAEA

Potential Impact for IAEA NWAL

- Results from FY21 $^{241}Am/^{241}Pu$ age dating method optimization can be shared with broader NWAL/IAEA or potentially through publication
- Project team is open to increased participation in round robin exercise if broader NWAL is interested and IAEA supports
  Note – this may require increased work scope
- First intercomparison testing the quality of ^{241}Am data produced for the IAEA – promote confidence in measurements
- Method optimization for bulk environmental swipes will support future age dating work with particle systems – lowering limits of detection, examining blanks, etc.

Thank you & Discussion

Questions sent by project team to IAEA:

- At the 2019 RANC Conference, the IAEA ESL presented results from initial work to develop a capability to separate and measure ^{241}Am from environmental samples. Is ESL still working to develop radiochemistry and mass spectrometry capabilities to measure ^{241}Am in environmental samples, or will they rely on the NWAL for these measurements?

- Is ESL interested in ^{241}Pu and ^{241}Am optimized methods for both TIMS and ICP, or are they only interested in ICP?

- Are there concentration ranges of Am on a cotton swipe where the IAEA would request an Am analysis? For example, would these analyses be requested for fg-level Am or only on larger samples with pg-level Am? (note - this will help us optimize our NWAL Am methods)